Ionic liquids

Field of the Invention

The invention relates to ionic liquids for use in electrochemical cells and organic syntheses.

Solvent-free ionic liquids or "salts which are molten at room temperature" were described for the first time in US 2446331. The problem with these strong Lewis acids is the formation of toxic gases on contact with atmospheric moisture.

Compounds involving $AlCl_3$ and 1-ethyl-3-methylimidazolium (EMI) chloride have been investigated for a long time. Wilkes and Zaworotko presented novel solvent-free ionic liquids, EMI BF_4 and EMI O_2CCH_3, in 1992 in J. Chem. Soc., Chem. Commun., p. 965. However, these compounds are unsuitable for use as electrolyte in electrochemical cells since the BF_4^- and $CH_3CO_2^-$ anions are oxidised even at relatively low potentials.

WO 98/07729, incorporated herein by reference, describes a new class of conductive salts, the lithium borate complexes. These compounds have shown particularly good results in cycling experiments and have proven particularly stable. The borate salts are in the solid state and thus have relatively low conductivity.

US 5827602, incorporated herein by reference, describes the use of ionic liquids from the group consisting of pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazoleium, pyrazolium, thiazolium, oxazolium and triazolium salts in electrochemical cells. These ionic liquids are particularly suitable for this application owing to good conductivities. The crucial disadvantage consists in the expensive synthesis of the raw materials, in particular the anions.

[illegible] which have a large liquid range, high thermal stability and low corrosivity and anions which are less expensive to synthesise

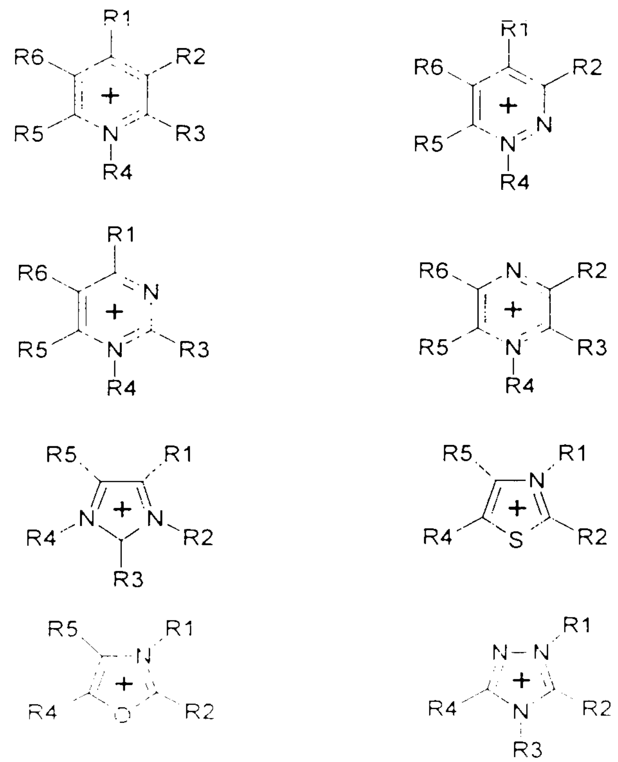
Upon further study of the specification and appended claims, further objects and advantages of this invention will become apparent to those skilled in the art.

These objects are achieved by ionic liquids of the general formula

$$K^+A^- \qquad (I)$$

in which:

K^+ is a cation selected from the group consisting of



where

R^1 to R^5 are identical or different and are each individually

- an alkyl radical (C_1 to C_8), which is unsubstituted or partially or fully substituted by further groups, preferably F, Cl, $N(C_nF_{(2n+1-x)}H_x)_2$, $O(C_nF_{(2n+1-x)}H_x)$, $SO_2(C_nF_{(2n+1-x)}H_x)$ or $C_nF_{(2n+1-x)}H_x$ where $1<n<6$ and $0<x\leq 13$,

- a phenyl radical which is unsubstituted or partially or fully substituted by further groups, preferably F, Cl, $N(C_nF_{(2n+1-x)}H_x)_2$, $O(C_nF_{(2n+1-x)}H_x)$, $SO_2(C_nF_{(2n+1-x)}H_x)$ or $C_nF_{(2n+1-x)}H_x$ where $1<n<6$ and $0<x\leq 13$, or

- one or more pairs of adjacent R^1 to R^6 can also be an alkylene or alkenylene radical having up to 8 C atoms and which is unsubstituted or partially or fully substituted by further groups, preferably halogen (such as F and Cl), $N(C_nF_{(2n+1-x)}H_x)_2$, $O(C_nF_{(2n+1-x)}H_x)$, $SO_2(C_nF_{(2n+1-x)}H_x)$ or $C_nF_{(2n+1-x)}H_x$ where $1<n<6$ and $0<x\leq 13$; and

A^- is an anion selected from

$[B(OR^7)_n(OR^8)_m(OR^9)_o(OR^{10})_p]^-$

where

$0\leq n, m, o, p\leq 4$, and $m+n+o+p=4$, and

R^7 to R^{10} are different or identical and are each, individually,

an aromatic ring selected from phenyl, naphthyl, anthracenyl and phenanthrenyl, which is unsubstituted or monosubstituted or polysubstituted by $C_nF_{(2n+1-x)}H_x$ where $1<n<6$ and $0<x\leq 13$, or halogen (F, Cl or Br),

an aromatic heterocyclic ring selected from pyridyl, pyrazyl and pyrimidyl, which is unsubstituted or monosubstituted or

an alkyl radical (C_1 to C_8), which is unsubstituted or partially or fully substituted by further groups, preferably F, Cl, , $N(C_nF_{(2n+1-x)}H_x)_2$,

$O(C_nF_{(2n+1-x)}H_x)$, $SO_2(C_nF_{(2n+1-x)}H_x)$, or $C_nF_{(2n+1-x)}H_x$ where $1<n<6$ and $0<x\leq 13$; or

one or more pairs of R^7 to R^{10} can also form

an aromatic ring selected from phenylene, naphthylene, anthracenylene and phenanthrenylene, which is unsubstituted or monosubstituted or polysubstituted by $C_nF_{(2n+1-x)}H_x$, where $1<n<6$ and $0<x\leq 13$, or halogen (F, Cl or Br),

an aromatic heterocyclic ring selected from pyridylene, pyrazylene and pyrimidylene, which is unsubstituted or monosubstituted or polysubstituted by $C_nF_{(2n+1-x)}H_x$, where $1<n<6$ and $0<x\leq 13$, or halogen (F, Cl or Br), or

an alkylene or alkenylene radical having up to 8 C atoms and which is unsubstituted or partially or fully substituted by further groups, preferably halogen (such as F and Cl), $N(C_nF_{(2n+1-x)}H_x)_2$, $O(C_nF_{(2n+1-x)}H_x)$, $SO_2(C_nF_{(2n+1-x)}H_x)$ or $C_nF_{(2n+1-x)}H_x$ where $1<n<6$ and $0<x\leq 13$; or

or OR^7 to OR^{10},

individually or together, are an aromatic (having, e.g., 6 to 14 C atoms) or aliphatic (having, e.g., 1 to 6 C atoms) carboxyl, dicarboxyl, oxysulfonyl or oxycarbonyl radical, which is unsubstituted or partially or fully substituted by further groups, preferably F, Cl, $N(C_nF_{(2n+1-x)}H_x)_2$, $O(C_nF_{(2n+1-x)}H_x)$, $SO_2(C_nF_{(2n+1-x)}H_x)$ or $C_nF_{(2n+1-x)}H_x$, where $1<n<6$ and $0<x\leq 13$.

These ionic liquids are suitable as solvents in organic synthesis, but also for use in electrochemical cells. In addition, the ionic liquids are suitable for use in the catalysis of chemical reactions. In addition, they can be used as inert solvents for highly reactive chemicals. A further area is use as hydraulic liquid.

anode, a separator and an electrolyte. In general, electrochemical capacitors comprise two electrodes, a separator and an electrolyte. See, e.g., Figures 3 and 4 of U.S. 5,827,602

It has been found that the compounds according to the invention are hydrophobic. Furthermore, the anhydrous synthesis minimises the undesired introduction of water into the system.

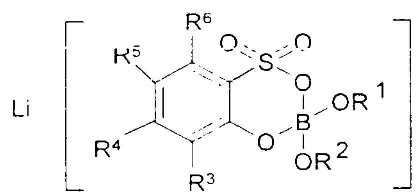
Surprisingly, it has been found that the ionic liquids do not corrode, but instead even passivate the aluminium current collector usually used in electrochemical cells. This enables the cycle stability to be increased. In addition, improved thermal stability of the system through the use of ionic liquids has been observed.

It has been found that the addition of solvents of low viscosity enables the conductivity to be improved. Low viscosity together with high conductivity is the prerequisite for use in electrochemical cells. The compounds according to the invention have a large liquid range, making them particularly suitable for these applications.

A prerequisite for use in double layer capacitors is high conductivity. The compounds according to the invention satisfy this criterion. The compounds according to the invention can be employed, alone or in mixtures with other solvents or conductive salts, in electrochemical cells, for the catalysis of chemical reactions or as hydraulic fluids. Suitable solvents are those selected from the group consisting of organic carbonates (for example ethylene carbonate, propylene carbonate and derivatives thereof, butylene carbonate, dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate, etc.), organic carboxylic acid esters (for example γ-butyrolactone, methyl formate, methyl acetate, ethyl acetate, ethyl propionate, methyl propionate, methyl butyrate, ethyl butyrate, etc.), organic carboxylic acid amides (for example dimethylformamide, methylformamide, formamide, etc.), organic ethers (for example 1,2-dimethoxyethane, tetrahydrofuran, 2-methyltetrahydrofuran, tetrahydrofuran derivatives, 1,3-dioxolane, dioxane, dioxolane derivatives, etc.) or other aprotic solvents (for [illegible] acetonitrile, sulfolane, dimethyl sulfoxide, nitromethane [illegible] example, ethylene carbonate/dimethyl carbonate (EC/DMC).

The compounds according to the invention can be used in electrolytes with conventional conductive salts. Examples of suitable electrolytes are those with conductive salts selected from $LiPF_6$, $LiBF_4$, $LiClO_4$, $LiAsF_6$, $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$ and $LiC(CF_3SO_2)_3$, and mixtures thereof. The electrolytes may also comprise organic isocyanates (DE 199 44 603) for reducing the water content.

Lithium complex salts of the following formula (DE 199 32 317) can also be present in the electrolyte composition



where

R^1 and R^2 are identical or different, are optionally bonded directly to one another via a single or double bond, and are each, individually or together, an aromatic ring from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or mono- to hexasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl or Br),

or are each, individually or together, an aromatic heterocyclic ring from the group consisting of pyridyl, pyrazyl and pyrimidyl, which may be unsubstituted or mono- to tetrasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl or Br),

or are each, individually or together, an aromatic ring from the group consisting of hydroxybenzocarboxyl, hydroxynaphthalenecarboxyl, hydroxybenzosulfonyl and hydroxynaphthalenesulfonyl, which may be unsubstituted or mono- to tetrasubstituted by alkyl (C_1 to C_6), alkoxy

[illegible] directly to one another by a single or double bond, have the following meanings:

1. alkyl (C_1 to C_6), alkoxy (C_1 to C_6) or halogen (F, Cl or Br)

2. an aromatic ring from the groups

phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or mono- to hexasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl or Br),

pyridyl, pyrazyl and pyrimidyl, which may be unsubstituted or mono- to tetrasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl or Br).

These compounds can be prepared by the following process (DE 199 32 317):

a) chlorosulfonic acid is added to 3-, 4-, 5- or 6-substituted phenol in a suitable solvent,

b) the intermediate from a) is reacted with chlorotrimethylsilane, and the reaction mixture is filtered and subjected to fractional distillation,

c) the intermediate from b) is reacted with, for example, lithium tetramethoxyborate(1-) in a suitable solvent, and the end product is isolated therefrom.

The electrolytes may likewise comprise compounds of the following formula (DE 199 41 566):

$$[([R^1(CR^2R^3)_k]_lA_x)_yKt]^+ \quad {}^-N(CF_3)_2$$

where

Kt = N, P, As, Sb, S or Se

H, halogen, substituted and/or unsubstituted alkyl C_nH_{2n+1}, substituted and/or unsubstituted alkenyl having 1-18 carbon atoms and one or more double bonds, substituted and/or unsubstituted alkynyl having 1-18 carbon atoms and one or more triple bonds, substituted and/or unsubstituted cycloalkyl C_mH_{2m-1}, mono- or polysubstituted and/or unsubstituted phenyl, or substituted and/or unsubstituted heteroaryl,

A may be included in R^1, R^2 and/or R^3 in various positions,

Kt may be included in a cyclic or heterocyclic ring,

the groups bonded to Kt may be identical or different,

where

n = 1-18

m = 3-7

k = 0 or 1-6

l = 1 or 2 in the case where x = 1 and 1 in the case where x = 0

x = 0 or 1

y = 1-4.

The process for the preparation of these compounds is characterised in that an alkali metal salt of the general formula

$$D^+ \ {}^-N(CF_3)_2$$

where D^+ is selected from the group of alkali metals, is reacted, in a polar organic solvent, with a salt of the general formula

$$[([R^1(CR^2R^3)_k]_lA_x)_yKt]^+ \ {}^-E$$

Kt, A, R^1, R^2, R^3, k, l, x and y are as defined above, and

${}^-E$ is F^-, Cl^-, Br^-, I^-, BF_4^-, ClO_4^-, AsF_6^-, SbF_6^- or PF_6^-

However, use can also be made of electrolytes comprising compounds of the general formula (DE 199 53 638)

$$X\text{-}(CYZ)_m\text{-}SO_2N(CR^1R^2R^3)_2$$

where

X is H, F, Cl, C_nF_{2n+1}, C_nF_{2n-1} or $(SO_2)_kN(CR^1R^2R^3)_2$

Y is H, F or Cl

Z is H, F or Cl

R^1, R^2 and R^3 are H and/or alkyl, fluoroalkyl or cycloalkyl having up to 9 C atoms

m is 0-9 and, if X = H, $m \neq 0$

n is 1-9

k is 0 if m = 0 and k = 1 if m = 1-9,

These compounds can be prepared by reacting partially or perfluorinated alkylsulfonyl fluorides with dimethylamine in organic solvents.

Use can also be made of electrolytes comprising complex salts of the general formula (DE 199 51 804)

$$M^{x+}[EZ]^{y-}_{x/y}$$

in which:

x and y are 1, 2, 3, 4, 5 or 6

M^{x+} is a metal ion

$BR^1R^2R^3$, $AlR^1R^2R^3$, $PR^1R^2R^3R^4R^5$, $AsR^1R^2R^3R^4R^5$ and $VR^1R^2R^3R^4R^5$.

R^1 to R^5 are identical or different, are optionally bonded directly to one another by a single or double bond, and each, individually or together, are

a halogen (F, Cl or Br),

an alkyl or alkoxy radical (C_1 to C_8), which may be partially or fully substituted by F, Cl or Br,

an aromatic ring, optionally bonded via oxygen, selected from the group phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or mono- to hexasubstituted by alkyl (C_1 to C_8) or F, Cl or Br,

an aromatic heterocyclic ring, optionally bonded via oxygen, selected from the group pyridyl, pyrazyl and pyrimidyl, which may be unsubstituted or mono- to tetrasubstituted by alkyl (C_1 to C_8) or F, Cl or Br, and

Z is OR^6, NR^6R^7, $CR^6R^7R^8$, OSO_2R^6, $N(SO_2R^6)(SO_2R^7)$, $C(SO_2R^6)(SO_2R^7)(SO_2R^8)$ or $OCOR^6$, where

R^6 to R^8 are identical or different, are optionally bonded directly to one another by a single or double bond and are each, individually or together,

hydrogen or as defined for R^1 to R^5.

These compounds can be prepared by reacting a corresponding boron or phosphorus Lewis acid/solvent adduct with a lithium or tetra-alkylammonium imide, methanide or triflate.

The electrolyte composition can also contain borate salts (DE 199 59

722) of the general formula

in which:

M is a metal ion or tetraalkylammonium ion,

x and y are 1, 2, 3, 4, 5 or 6,

R^1 to R^4 are identical or different and are alkoxy or carboxyl radicals (C_1-C_8), which are optionally bonded directly to one another by a single or double bond.

These borate salts are prepared by reacting lithium tetraalkoxyborate or a 1:1 mixture of lithium alkoxide with a borate with a suitable hydroxyl or carboxyl compound in a ratio of 2:1 or 4:1 in an aprotic solvent.

The compounds according to the invention may also be employed in electrolytes comprising lithium fluoroalkylphosphates of the general formula

$$Li^+[PF_x(C_yF_{2y+1-z}H_z)_{6-x}]^-$$

in which

$1 \leq x \leq 5$

$3 \leq y \leq 8$

$0 \leq z \leq 2y + 1$

and the ligands ($C_yF_{2y+1-z}H_z$) may be identical or different, with the exception of the compounds of the general formula

e is an integer from 1 to 4, with the provisos that b and c are not simultaneously each = 0, and the sum a + e is equal to 6, and the ligands $(CH_bF_c(CF_3)_d)$ may be identical or different (DE 100 089 55). The process for the preparation of lithium fluoroalkylphosphates of the above-mentioned formula is characterised in that at least one compound of the general formula

$H_mP(C_nH_{2n+1})_{3-m}$,

$OP(C_nH_{2n+1})_3$,

$Cl_mP(C_nH_{2n+1})_{3-m}$,

$F_mP(C_nH_{2n+1})_{3-m}$,

$Cl_oP(C_nH_{2n+1})_{5-o}$,

$F_oP(C_nH_{2n+1})_{5-o}$,

in each of which

$0 \leq m \leq 2$, $3 \leq n \leq 8$ and $0 \leq o \leq 4$,

is fluorinated by electrolysis in hydrogen fluoride, the resultant mixture of fluorination products is separated by extraction, phase separation and/or distillation, and the resultant fluorinated alkyl-phosphorane is reacted with lithium fluoride in an aprotic solvent mixture with exclusion of moisture, and the resultant salt is purified and isolated by conventional methods.

The compounds according to the invention can be employed in electrolytes for electrochemical cells which contain positive-electrode material of coated metal cores selected from the group of Sb, Bi, Cd, In, Pb, Ga and tin or alloys thereof (DE 100 16 024). The process for the production of this positive-electrode material is characterised in

a) a suspension or sol of the metal or alloy core in urotropin is prepared.

b) the suspension is emulsified with C_5-C_{12}-hydrocarbons,

c) the emulsion is precipitated onto the metal or alloy cores, and

d) the metal hydroxides or oxyhydrides are converted into the corresponding oxide by heat-treatment of the system.

The compounds according to the invention can also be employed in electrolytes for electrochemical cells having negative electrodes made from common lithium intercalation and insertion compounds, but also with negative-electrode materials made of lithium mixed oxide particles coated with one or more metal oxides (DE 199 22 522) by suspending the particles in an organic solvent, adding a solution of a hydrolysable metal compound and a hydrolysis solution to the suspension, and then filtering off, drying and optionally calcining the coated particles. They can also made of lithium mixed oxide particles coated with one or more polymers (DE 199 46 066), obtained by a process in which the particles are suspended in a solvent, and the coated particles are subsequently filtered off, dried and optionally calcined. The compounds according to the invention may likewise be employed in systems having negative electrodes made of lithium mixed oxide particles with one or more coatings of alkali metal compounds and metal oxides (DE 100 14 884). The process for the production of these materials is characterised in that the particles are suspended in an organic solvent, an alkali metal salt compound suspended in an organic solvent is added, metal oxides dissolved in an organic solvent are added, a hydrolysis solution is added to the suspension, and the coated particles are subsequently filtered off, dried and calcined.

A general example of the invention is explained in greater detail below.

where

$0 \leq n, m, o, p \leq 4$, and $m+n+o+p=4$, and

R^7 to R^{10} are different or identical and are each, individually,

an aromatic ring selected from phenyl, naphthyl, anthracenyl and phenanthrenyl, which is unsubstituted or monosubstituted or polysubstituted by $C_nF_{(2n+1-x)}H_x$, where $1<n<6$ and $0<x\leq 13$, or halogen (F, Cl or Br),

an aromatic heterocyclic ring selected from pyridyl, pyrazyl and pyrimidyl, which is unsubstituted or monosubstituted or polysubstituted by $C_nF_{(2n+1-x)}H_x$, where $1<n<6$ and $0<x\leq 13$, or halogen (F, Cl or Br), or

an alkyl radical (C_1 to C_8), which is unsubstituted or partially or fully substituted by further groups, preferably F, Cl, , $N(C_nF_{(2n+1-x)}H_x)_2$, $O(C_nF_{(2n+1-x)}H_x)$, $SO_2(C_nF_{(2n+1-x)}H_x)$, or $C_nF_{(2n+1-x)}H_x$, where $1<n<6$ and $0<x\leq 13$; or

one or more pairs of R^7 to R^{10} can also form

an aromatic ring selected from phenylene, naphthylene, anthracenylene and phenanthrenylene, which is unsubstituted or monosubstituted or polysubstituted by $C_nF_{(2n+1-x)}H_x$, where $1<n<6$ and $0<x\leq 13$, or halogen (F, Cl or Br),

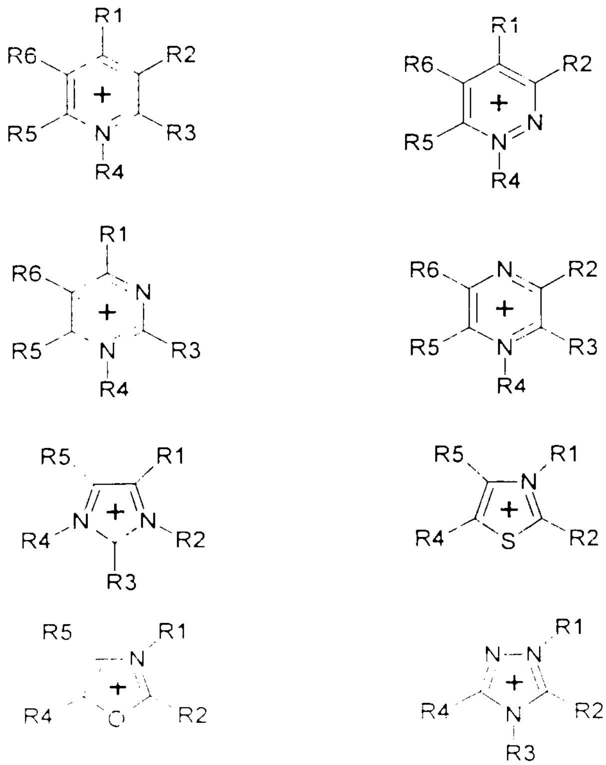
an aromatic heterocyclic ring selected from pyridylene, pyrazylene and pyrimidylene, which is unsubstituted or monosubstituted or polysubstituted by $C_nF_{(2n+1-x)}H_x$, where $1<n<6$ and $0<x\leq 13$, or halogen (F, Cl or Br), or

an alkylene or alkenylene radical having up to 8 C atoms and which is unsubstituted or partially or fully substituted by further groups, preferably halogen (such as F and Cl), $N(C_nF_{(2n+1-x)}H_x)_2$, $O(C_nF_{(2n+1-}$

individually or together, are an aromatic (having, e.g., 6 to 14 C atoms) or aliphatic (having, e.g., 1 to 6 C atoms) carboxyl, dicarboxyl, oxysulfonyl or oxycarbonyl radical, which is unsubstituted or partially or fully substituted by further groups, preferably F, Cl, $N(C_nF_{(2n+1-x)}H_x)_2$, $O(C_nF_{(2n+1-x)}H_x)$, $SO_2(C_nF_{(2n+1-x)}H_x)$ or $C_nF_{(2n+1-x)}H_x$, where $1<n<6$ and $0<x\leq 13$,

a known process from WO 98/07729 is used.

In order to prepare the cation selected from the group consisting of



a known process from US 5827602 is used. The starting materials are reacted for from about 0.5 to 12 hours, preferably 1-4 hours, in an aprotic organic solvent, at temperatures in the liquid range of the solvent

[illegible] example to from [illegible] in the case of [illegible] as by-product. and the by-product which precipitates out is filtered off. preferably filtered off by vacuum

The solvent/product mixture can be employed directly in the electrolyte. If desired, the solvent can also be distilled off and the resultant product dried.

The examples below are intended to explain the invention in greater detail, but without representing a limitation.

In the foregoing and in the following examples, all temperatures are set forth uncorrected in degrees Celsius; and, unless otherwise indicated, all parts and percentages are by weight.

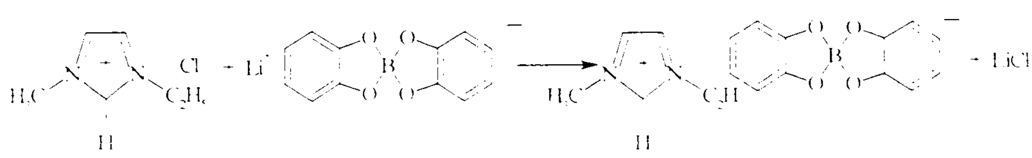
The entire disclosure of all applications, patents and publications, cited above and below, and of corresponding German Application No. 100 26 565.0 filed May 30, 2000 is hereby incorporated by reference.

<u>Examples</u>

<u>Example 1</u>

Synthesis of 1-ethyl-3-methylimidazolium bis[1,2-benzenediolato-O,O']borate

Lithium bis[1,2-benzenediolato-O,O']borate is synthesised in accordance with WO 94/27335 or WO 98/07729. The product is reacted in acetonitrile in accordance with the following reaction equation:



is distilled off under reduced pressure and the resultant 1-ethyl-3-methylimidazolium bis[1.2-benzenediolato-O.O']borate is dried under reduced pressure.

<u>Example 2</u>

Synthesis of 1-ethyl-3-methylimidazolium bis[salicylato]borate

Lithium bis[salicylato]borate is synthesised in accordance with WO 94/27335 or in accordance with WO 98/07729 and reacted with 1-ethyl-2-methylimidazolium chloride in acetonitrile. The reaction mixture is filtered by vacuum through a glass frit with cooling in order to remove the LiCl formed as by-product. The solvent is distilled off under reduced pressure, and the resultant 1-ethyl-3-methylimidazolium bis[salicylato]borate is dried under reduced pressure.

<u>Example 3</u>

Synthesis of 1-ethyl-3-methylimidazolium bis[oxalato]borate

Lithium bis[oxalato]borate is synthesised in accordance with WO 94/27335 or in accordance with WO 98/07729 and reacted with 1-ethyl-2-methylimidazolium chloride in acetonitrile. The reaction mixture is filtered by vacuum through a glass frit with cooling in order to remove the LiCl formed as by-product. The solvent is distilled off under reduced pressure, and the resultant 1-ethyl-3-methylimidazolium bis[oxalato]borate is dried under reduced pressure.

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

departing from the spirit and scope thereof, can make various

changes and modifications of the invention to adapt it to various usages and conditions.